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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

ON THE APPLICABILITY OF THE LAW OF CORRESPONDING STATES TO THE JOULE-THOMSON EFFECT IN WATER AND CARBON DIOXIDE.

BY HARVEY N. DAVIS.

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In the classical plug experiments of Joule and Kelvin certain gases were forced by pressure through a porous plug under circumstances which permitted the accurate measurement of any small resulting change in their temperature. It can easily be shown that a perfect gas would show no such change. As a matter of fact, hydrogen was found to be slightly warmer on the low pressure side of such a plug than on the high pressure side, while air, oxygen, nitrogen and carbon dioxide were slightly cooler. The ratio of the observed drop in temperature to the drop in pressure in such a plug has ever since been called the Joule-Thomson coefficient.

The results of such experiments afford the best known means of computing corrections for reducing the temperature scale of a gas thermometer to Kelvin's absolute thermodynamic scale. For this purpose one must know the Joule-Thomson coefficient of the gas in the thermometer at all temperatures between 0° C. and the t° C. at which the correction is desired. Unfortunately, none of the experiments either of Joule and Kelvin or of any of their successors are at temperatures other than between 0° C. and 100° C., except for certain inversion points of Olschewsky obtained under circumstances not yet fully understood. These are not enough to give a direct determination of the absolute thermodynamic scale above 100°. In order to get one indirectly, it has been customary to assume that, at least in the five gases, hydrogen, oxygen, nitrogen, carbon dioxide and air, the Joule-Thomson effect obeys the law of corresponding states. That is, it is assumed that if the coefficient for each gas is expressed in terms of the critical pressure and temperature of that gas as units, and if the results are plotted against the temperature expressed in the same

"reduced" units, the resulting curves will be identical for all five gases. The observations at ordinary temperatures on hydrogen, whose critical temperature is very low, will then correspond to observations at very high temperatures on other gases, and will afford a useful though precarious extrapolation of their curves to above 1000° C.

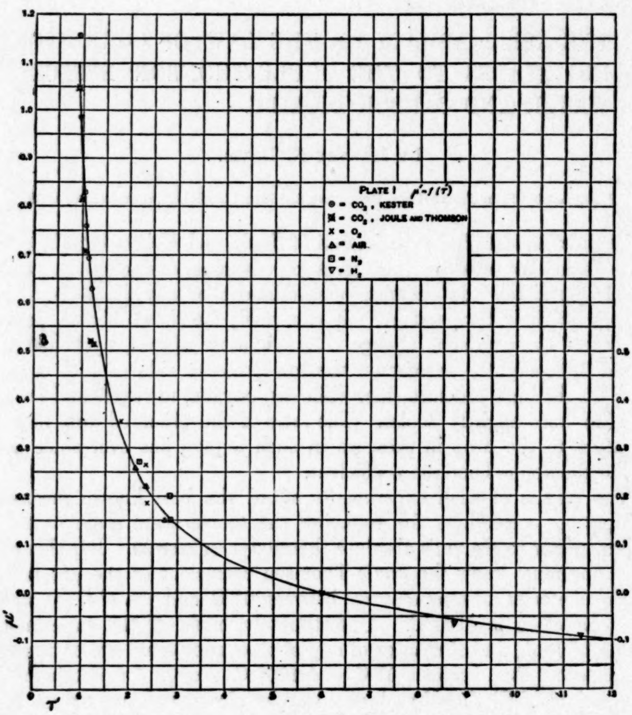

FIGURE 1. Reduced Joule-Thomson coefficient, μ', plotted against reduced temperature. From Buckingham's paper in the Bulletin of the Bureau of Standards, May, 1908. (See the note at the end of this paper.)

The experimental justification of this use of the law of corresponding states is, as yet, meager. Figure 1, which is taken from a recent paper by Buckingham, represents the available data. It will be seen that neither the hydrogen nor the carbon dioxide observations overlap those on the other three gases, and that the points for each of these

three gases show such discrepancies among themselves as to make uncertain any judgment as to their agreement with each other. What evidence there is, is in favor of the validity of the law of corresponding states; but an accurate verification of it, especially for two substances with very different critical temperatures, would put the whole subject on a much more satisfactory basis.

In this paper it will be shown that this law is verified for carbon dioxide and water within the limit of error of the available observations on water. This limit of error is unfortunately quite as great as that of the oxygen, nitrogen and air observations plotted in Figure 1. Nevertheless, a multiplication of evidence, even of an inferior sort, is often valuable, and in this case there is an added interest because, if water, which is known to be anomalous in many ways through association, is found to obey the law of corresponding states as to its Joule-Thomson effect, it is probable that the permanent gases will also obey that law.

There are four sets of experiments on water which can be used. They were all undertaken for the purpose of determining the variation of the specific heat of superheated steam with pressure and temperature, an investigation which has since been more satisfactorily accomplished in other ways. Of the four observers, Griessmann [1] used a porous plug very much like that of Joule and Thomson, while the other three, Grindley, [2] Peake [3] and Dodge,[4] used what engineers call a throttling or wiredrawing calorimeter. The essential part of this instrument is a small orifice through which the steam flows tumultuously from one chamber into another, the high velocity of the steam being subsequently destroyed by friction at the surfaces of the walls of the second chamber and within the steam itself. During this process the kinetic energy of the steam is transformed into heat, all of which, if the thermal insulation is perfect, goes back into the steam. If this transformation is complete, the throttling calorimeter is exactly equivalent to a porous plug. To ensure this completeness, one of the three observers (Peake) put a quantity of wire gauze in the path of the steam from the orifice, and another (Dodge) used at times four small orifices instead of one larger one without noticeable change in the results. Grindley took no especial precautions of this sort, but the

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[1] Zeitsch. Ver. d. Ing., 1903, **47**, 1852 and 1880; also Forschungsarb., Ver. d. Ing., 1904, **13**, 1.

[2] Phil. Trans., 1900–1, **194A**, 1.

[3] Proc. Roy. Soc., 1905, A, **76**, 185.

[4] Jour. Am. Soc. Mech. Engs., 1907, **28**, 1265; and 1908, **30**, 1227.

fact that his results agree with those of Peake and of Griessmann shows that none were necessary in his apparatus.

This agreement is in many other ways a significant one, for it is inconceivable in view of the great differences in almost every respect between the details of the three sets of apparatus, that any serious systematic errors should have been present in any one of the sets of results without completely destroying the agreement between them. This is particularly true in the matter of heat insulation, where the precautions taken by the three observers had almost nothing in common except effectiveness. In Dodge's work also this point was carefully considered but the results are not so satisfactory. They will be discussed and a correction computed on page 262.

In all four cases the thermometry is the weakest part of the work. It is especially unfortunate for the present purpose that the original aim of the experiments did not require or suggest that the difference between the temperatures before and after the expansion be measured as such, as by a thermocouple or a differential resistance thermometer. The subtraction which must now be made of one reading on a mercury thermometer from another reading on another thermometer, to give a small difference, is not a particularly accurate method of getting that difference. The same is true of the determination of the pressure drop. The individual measurements were comparatively good, being made in three of the cases with carefully calibrated Bourdon or spring gauges, and in the fourth case by an extra measurement of the temperature of resaturation of the low side steam, but the differences needed in this paper must inevitably be subject to comparatively large errors. The reader must therefore be prepared for much lack of self-consistency in the results. It is hoped that the errors are largely incidental errors such as can be eliminated by averaging.

Grindley's experiments were performed in England during the winter of 1897–8. His data are given in full in his paper and are plotted in his Diagram 5 reproduced here as Figure 2. It will be observed that in every case his steam drops several pounds in pressure before it leaves the saturation line. This he explained by means of a curious and now discredited "heat of gasification." A better explanation is that his steam was initially slightly wet. Since this source of error affects the high side data of every one of his experiments, it might seem that all of his work must be rejected. It will be noticed, however, that his experiments are grouped into runs; that is, if in a certain experiment steam in a certain initial condition has been throttled to a certain low side pressure and temperature, then in later experiments of the same group, steam *in the same initial condition* is more and more throttled

to lower low side pressures and temperatures, which when plotted together form the throttling curves of Figure 2. Since it is characteristic of throttling that the total heat, H, of the steam is the same on the high and low sides, it follows that H is constant along the whole of any throttling curve, and that any two low side points of a run may be taken, one as describing the high side conditions and the other as describing the low side conditions of a possible throttling experiment.

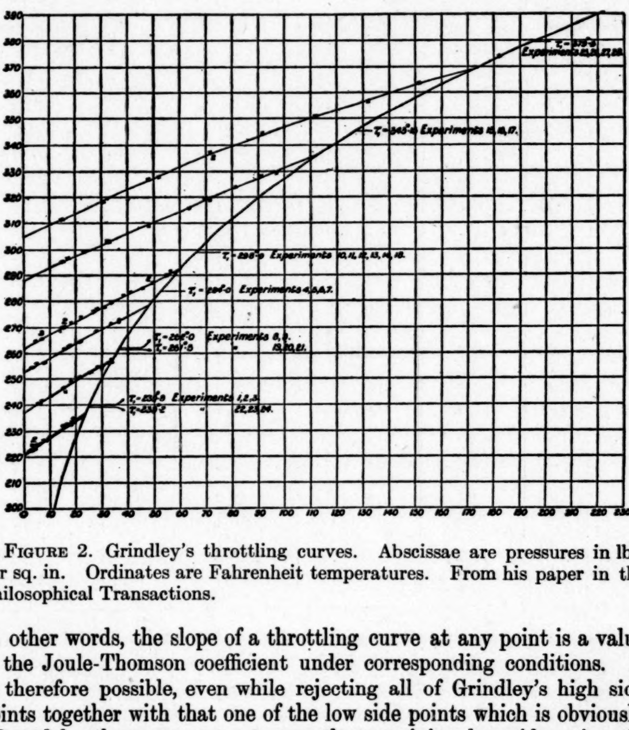

FIGURE 2. Grindley's throttling curves. Abscissae are pressures in lbs. per sq. in. Ordinates are Fahrenheit temperatures. From his paper in the Philosophical Transactions.

In other words, the slope of a throttling curve at any point is a value of the Joule-Thomson coefficient under corresponding conditions. It is therefore possible, even while rejecting all of Grindley's high side points together with that one of the low side points which is obviously affected by the same error, to use the remaining low side points in pairs. There were 101 of them in all, lying on seven throttling curves. They were first grouped so as to give 29 average points, the averaging being justified by the fact that for a range of not more than 5°, a throttling curve can be considered straight. These means were then taken two by two consecutively to give 22 values of the Joule-Thomson

coefficient, each of which is assumed to correspond to the mean of the high and low side temperatures from which it was obtained. The values of the coefficient have been "reduced" by multiplying by 2.56,

TABLE I.

SUMMARY OF GRINDLEY'S THROTTLING EXPERIMENTS.

Curve.	No. of Points.	Average Pressure		Average Temperature		Reduced Joule-Thomson Coefficient.
		lbs. per sq. in.	Reduced.	Fahr.	Reduced.	
A	1–1	141.6	0.0480	360.2	0.714	0.82
	1–2	121.7	0.0412	353.9	0.708	0.79
	2–1	101.6	0.0344	347.4	0.703	0.86
	1–2	81.7	0.0277	340.5	0.697	0.92
	2–2	61.0	0.0207	332.3	0.690	1.12
	2–1	40.3	0.0137	322.9	0.682	1.20
	1–1	22.7	0.0077	315.0	0.675	1.11
B	2–1	87.5	0.0296	326.3	0.685	1.00
	1–3	74.7	0.0253	321.0	0.680	1.13
	3–1	58.2	0.0197	313.6	0.673	1.15
	1–2	40.3	0.0137	306.1	0.667	1.00
	2–3	25.5	0.0086	299.9	0.662	1.14
C	3–5	50.7	0.0172	288.0	0.651	1.27
	5–4	37.5	0.0127	281.4	0.645	1.29
	4–8	24.3	0.0082	274.7	0.640	1.31
	8–4	12.4	0.0042	268.4	0.634	1.39
D	4–5	26.3	0.0089	267.2	0.633	1.40
	5–4	12.4	0.0042	259.5	0.626	1.47
E	8–5	24.2	0.0082	251.7	0.620	1.39
	5–4	12.8	0.0043	245.1	0.613	1.57
F *a*	6–7	12.2	0.0041	229.3	0.600	1.74
F *b*	6–5	11.5	0.0039	228.7	0.600	1.69

Column 2 indicates the number of observations involved in each of the two means used in each case. Thus 6–7 indicates that the mean used as the high side point of the pair included 6 of the points plotted in figure 2, while that used as the low side point involved 7.

a factor which is the ratio of the critical pressure of water expressed in pounds per square inch (2947 lbs. per sq. in. or 200 atmospheres [5]) to its critical temperature in Fahrenheit degrees absolute (1149° F. abs. or 365° C. ord.[5]). The results are summarized in Table I, which gives

[5] Cailletet and Colardeau, Jour. de Phys., 1891, **10**, 333.

also the corresponding "reduced" pressures and temperatures. These values of the coefficient are plotted as open circles in Figure 6.

The experiments of Griessmann were performed in the mechanical engineering laboratory of the "Technische Hochschule" in Dresden, and were published in 1903. They were primarily undertaken to test the heat of gasification hypothesis already mentioned, and are a critical

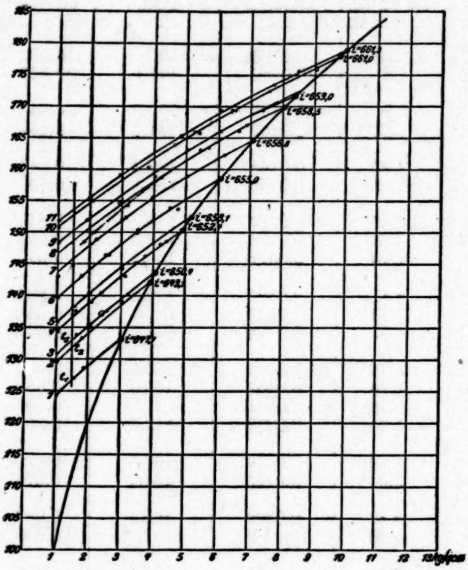

FIGURE 3. Griessmann's throttling curves. Abscissae are pressures in kg. per sq. cm. Ordinates are Centigrade temperatures. From his paper in the Forschungsarbeiten.

repetition of Grindley's work. The data are given in full in the paper in the Forschungsarbeiten, and are plotted in his Figure 7, which is reproduced here as Figure 3. He records 13 runs with 87 sets of low side observations, which with the 13 high side observations give 100 points on his diagram. Of these, three points on curve 2, one point on curve 7, three points on curve 8, and three points on curve 9 lie so far off the smooth curves determined by the neighboring points that they have arbitrarily been omitted from these calculations. The remaining 90 points, lying on 11 curves, have been grouped in 44 means

TABLE II.

Summary of Griessmann's Observations.

Curve.	No. of Points.	Average Pressure		Average Temperature		Reduced Joule-Thomson Coefficient.
		kgs./sq. cm.	Reduced.	Cent.	Reduced.	
1	2–2	2.19	0.0106	129.8	0.632	1.33
	2–1	1.37	0.0066	126.1	0.625	1.64
2	1–1	2.86	0.0138	137.6	0.644	1.34
	1–1	1.42	0.0069	131.4	0.634	1.56
3	2–2	2.97	0.0144	139.2	0.646	1.26
	2–2	1.81	0.0088	134.4	0.639	1.44
4	2–5	4.35	0.0210	148.2	0.660	1.19
	5–4	2.85	0.0138	142.3	0.651	1.30
	4–2	1.46	0.0071	136.5	0.642	1.47
5	1–1	4.11	0.0199	149.2	0.662	1.27
	1–1	2.53	0.0122	142.3	0.651	1.23
	1–1	1.52	0.0074	138.2	0.644	1.44
6	2–2	5.36	0.0260	156.1	0.673	1.07
	2–3	4.18	0.0202	152.2	0.667	1.06
	3–4	2.98	0.0144	147.9	0.660	1.22
	4–2	1.64	0.0079	142.5	0.651	1.42
7	2–2	5.56	0.0219	160.3	0.679	0.93
	2–3	3.64	0.0176	154.1	0.670	1.18
8	3–2	6.37	0.0308	165.4	0.687	0.88
	2–1	4.90	0.0237	161.0	0.680	1.08
9	1–2	6.46	0.0313	166.9	0.690	0.84
	2–1	3.73	0.0180	158.2	0.676	1.13
	1–1	1.46	0.0071	150.2	0.663	1.25
10	2–2	8.22	0.0398	174.1	0.701	0.88
	2–1	5.02	0.0243	164.7	0.686	0.99
	1–1	2.55	0.0123	156.8	0.673	1.23
	1–1	1.55	0.0075	152.8	0.668	1.29
11	1–2	9.05	0.0438	176.6	0.705	0.75
	2–2	7.17	0.0347	171.9	0.698	0.88
	2–1	5.53	0.0268	167.3	0.690	0.96
	1–1	3.89	0.0188	162.2	0.682	1.01
	1–1	2.48	0.0120	157.4	0.675	1.19
	1–1	1.52	0.0074	153.8	0.669	1.25

which have been used as above to give the 33 values of the Joule-Thomson coefficient which are presented in the following table. They are plotted as circles with diagonal crossbars in Figure 6. The reduction factor in this case is 0.324, Griessmann's pressures being in kilograms per square centimeter and his temperatures in Centigrade degrees.

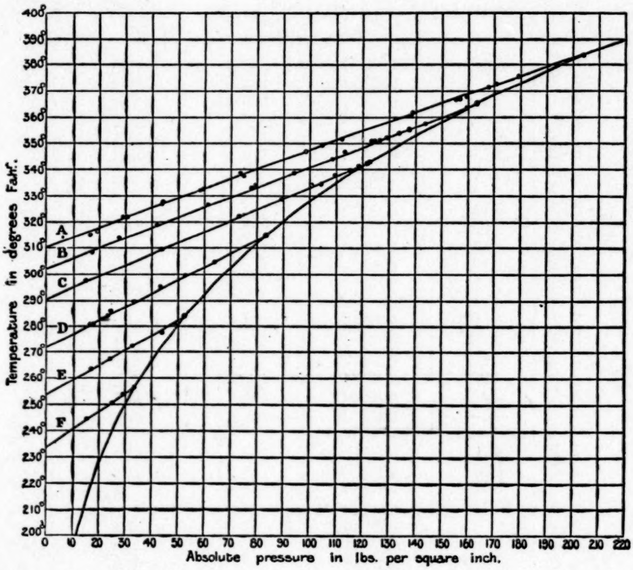

FIGURE 4. Peake's throttling curves. From his paper in the Proceedings of the Royal Society.

Peake's experiments were carried out in the engineering laboratory of Cambridge University in England and were begun in the fall of 1898. The appearance in 1900 of Grindley's work along almost identical lines at first inclined Peake to discontinue his investigation, but a careful examination of Grindley's data as compared with his own, led him to the discovery in both of the heat of gasification error already mentioned and to its true explanation, and his experiments were continued with this particular point in view. His apparatus was therefore redesigned so as to bring the steam as quickly as possible from the boiler to the orifice to avoid condensation on the way, and he, like

TABLE III.

SUMMARY OF PEAKE'S THROTTLING EXPERIMENTS.

Curve.	No. of Points.	Average Pressure		Average Temperature		Reduced Joule-Thomson Coefficient.
		mm. of Hg.[1]	Reduced.	Cent.	Reduced.	
A	3–3	9724	0.0639	192.3	0.730	0.85
	3–3	8503	0.0569	187.8	0.722	0.94
	3–2	7632	0.0502	184.4	0.716	0.90
	2–3	6282	0.0413	179.4	0.709	0.87
	3–2	4617	0.0304	173.1	0.699	0.94
	2–4	3239	0.0213	167.8	0.690	0.87
	4–4	1925	0.0127	162.5	0.683	1.05
B	4–9	7594	0.0499	181.5	0.712	0.97
	9–3	6128	0.0403	175.6	0.703	0.97
	3–2	4735	0.0312	170.0	0.695	0.95
	2–2	3359	0.0221	164.3	0.686	1.01
	2–2	1914	0.0126	158.2	0.675	1.00
C	2–2	6162	0.0405	171.8	0.697	1.09
	2–2	5762	0.0379	170.0	0.694	1.10
	2–1	5017	0.0337	166.6	0.689	1.05
	1–1	4163	0.0274	162.8	0.683	1.13
	1–1	3030	0.0199	157.4	0.675	1.11
	1–1	1513	0.0100	150.6	0.665	1.06
D	1–1	4212	0.0277	156.6	0.674	1.05
	1–1	3960	0.0260	155.3	0.671	1.14
	1–1	3547	0.0233	153.4	0.668	1.11
	1–1	3035	0.0200	151.0	0.665	1.17
	1–1	2502	0.0165	148.3	0.661	1.17
	1–2	1984	0.0131	145.6	0.656	1.36
	2–1	1460	0.0096	142.7	0.652	1.29
	1–1	986	0.0065	140.0	0.648	1.53
E	2–1	2045	0.0135	135.4	0.640	1.41
	1–1	1468	0.0096	132.1	0.635	1.35
	1–1	1050	0.0069	129.6	0.631	1.44
F	1–1	1404	0.0092	122.2	0.619	1.66
	1–1	1044	0.0069	119.7	0.615	1.63

[1] All of Peake's pressures were computed from suitable temperature measurements by means of Regnault's steam table. As a special precaution they have been recomputed with the new table of Holborn and Henning, and are therefore left in the metric units in which they were thus found. The "reduction factor" to give μ' is 238.

Griessmann, practically eliminated the effect which Grindley had found. His results are plotted as his Figure 4 which is reproduced as Figure 4 of this paper. He records 10 runs with 68 low side observations, making 78 points in all. Two of the high side points and two of the low side points still show traces of the wet steam effect and have therefore been rejected. The other low side points are much more

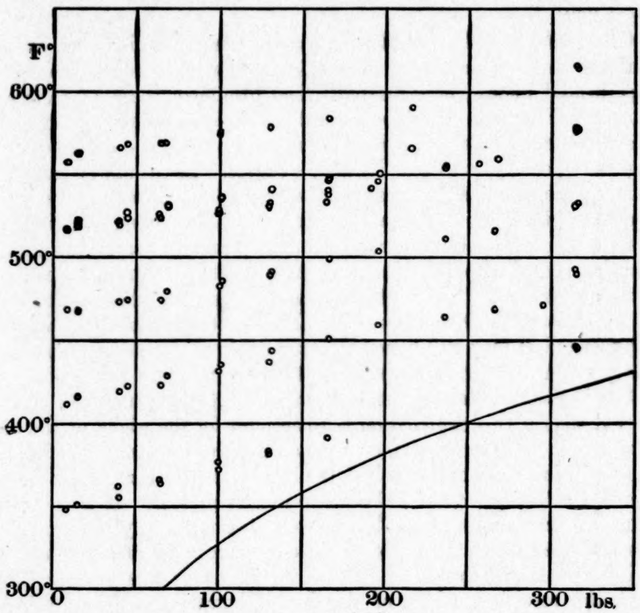

FIGURE 5. Dodge's throttling curves. Plotted from the original data sheets.

self-consistent than Griessmann's. The ten runs correspond to only six throttling curves. The 74 satisfactory points were grouped into 33 means, giving the 27 values of the Joule-Thomson coefficient which are presented in Table III and are plotted as circles with horizontal crossbars in Figure 6.

Dodge worked in the laboratories of the General Electric Company at Schenectady, N. Y., from 1901 to 1906. His data were not given at all in his first paper and were published only in part in his second

paper. What follows is based on a study of the original records, the generous loan of which for this purpose is very gratefully acknowledged. On his advice, the first 26 of his 92 runs were disregarded as preliminary, and 9 other runs were rejected, either because of experimental mishaps, or because the log did not show satisfactorily steady conditions. The data selected were corrected for probable radiation and conduction losses in the way explained in the appendix of this paper (page 262).

Of the 47 selected tests, 14 were like those already discussed, except that the temperatures were much higher, the high side steam being superheated instead of saturated. The results of these 14 tests are plotted in Figure 5. It will be noticed that in every case a smooth curve through the low side points runs considerably below the corresponding high side point, just as did Grindley's curves. In Grindley's case this was because the entering steam carried water in suspension, the presence of which made the true total heat of the incoming mixture less than its apparent total heat regarded as homogeneous saturated steam, and dropped all the low side points onto throttling curves lower than those on which they apparently belonged. A similar phenomenon may be in evidence in Dodge's case, for although the incoming steam was superheated, it may still have been carrying in suspension a part of the water which had been sprayed into it for temperature regulation just before it reached the high side chamber.[6] It must, however, be admitted that if this explanation is to account for the whole of the discrepancy in Dodge's results, an extraordinarily large amount of water in suspension must have reached the high side chamber — from one to one and a half per cent of the whole weight present. It is therefore probable that there is another source of error not yet discovered. Nevertheless, if the high side points are disregarded and the low side points are taken together in pairs as in Grindley's case, it is probable that the resulting values of the Joule-Thomson coefficient will be trustworthy.

Each of the 14 runs was handled separately. It did not seem best to take consecutive points together as in the other cases, because, at the very high temperatures here dealt with, the temperature difference between consecutive points is much smaller than at lower temperatures, and so an error in either observation would make much more difference in the coefficient. Furthermore, the throttling curves are more nearly straight in this range than at lower temperatures. The lowest point of a run has therefore been taken with the point just beyond the middle

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[6] See the work of Knoblauch and Jakob, Forschungsarb., 1906, **34**, 109.

TABLE IV.

Summary of Dodge's Throttling Curve Tests.

Test.	Average Pressure		Average Temperature		Reduced Joule-Thomson Coefficient.
	lbs. per sq. in.	Reduced.	Fahr.	Reduced.	
70 *a*	36.5	0.0124	563	0.892	0.52
	57.6	0.0196	569	0.895	0.39
	85.2	0.0289	572	0.899	0.36
70 *b*	54.2	0.0184	476	0.816	0.38
	73.0	0.0248	479	0.818	0.46
71	36.5	0.0124	356	0.711	0.72
	57.5	0.0195	362	0.716	0.62
	84.9	0.0288	369	0.722	0.75
72	36.5	0.0124	521	0.855	0.30
	57.4	0.0195	523	0.857	0.20
73	36.7	0.0125	418	0.765	0.55
	52.4	0.0178	424	0.770	0.48
	84.8	0.0288	248	0.774	0.44
74	54.0	0.0183	522	0.856	0.32
	72.6	0.0246	527	0.860	0.27
	102.2	0.0347	530	0.863	0.32
75	84.3	0.0286	373	0.726	0.58
	114.6	0.0389	381	0.733	0.52
76	127.3	0.0432	534	0.866	0.32
	101.0	0.0343	527	0.860	0.24
77	200.6	0.0681	547	0.877	0.50
	225.6	0.0765	551	0.881	0.44
78	57.5	0.0195	568	0.895	0.35
	105.0	0.0356	576	0.902	0.32
	142.0	0.0482	580	0.906	0.36
79	57.9	0.0196	527	0.860	0.50
	105.0	0.0356	535	0.867	0.49
	.142.0	0.0482	548	0.878	0.57
80	90.7	0.0308	535	0.867	0.43
	120.4	0.0409	539	0.870	0.39
	152.0	0.0516	543	0.874	0.34
	184.4	0.0626	548	0.878	0.35
81	90.3	0.0306	484	0.822	0.54
	120.3	0.0409	489	0.826	0.49
	152.0	0.0516	495	0.832	0.48
	184.0	0.0625	501	0.837	0.47
82	90.3	0.0306	434	0.779	0.57
	120.3	0.0409	441	0.785	0.62
	152.0	0.0516	447	0.790	0.54
	184.0	0.0625	452	0.795	0.52
	213.5	0.0724	458	0.800	0.42

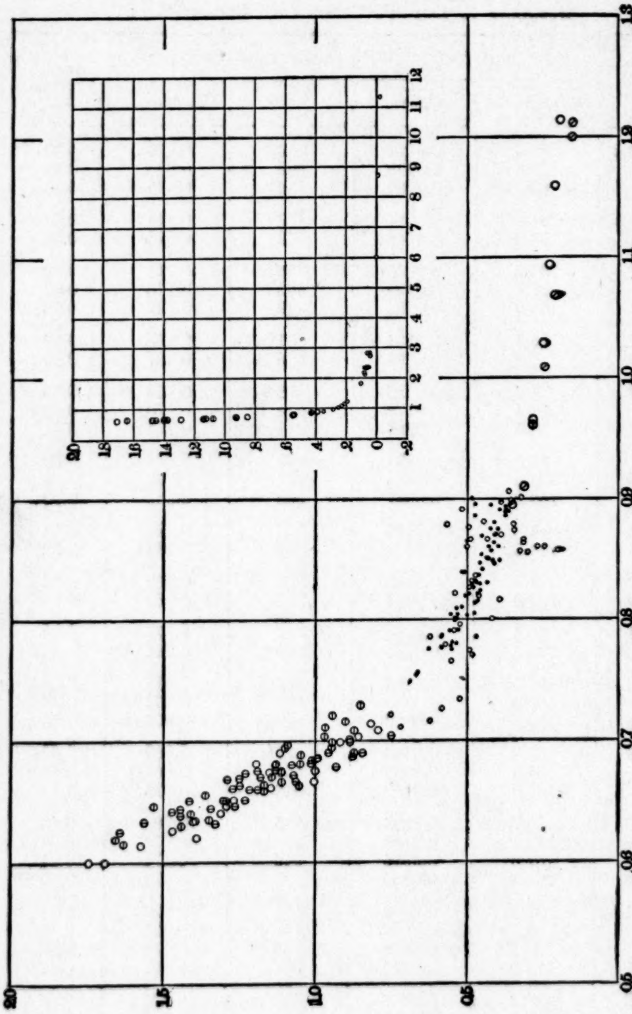

FIGURE 6. Reduced Joule-Thomson coefficient for steam and carbon dioxide plotted against reduced temperature. At the bottom are given the corresponding temperatures for steam on the Centigrade scale.

of that run, and so on, no point being used more than once. The 41 values of the coefficient obtained in this way are summarized in Table IV, and are plotted as small open circles in Figure 6. They lie in the range between 0.8 and 0.9 reduced temperature, filling a gap of considerable importance in that figure.

The remaining 33 of the selected runs cannot be handled in the same simple way, because the experiments which make up each of these runs are not so related as to give throttling curves, but are related in another way much better suited to the original purpose of the work, but much less suited to the present purpose. Nevertheless the gap between 0.7 and 0.9 in Figure 6 is so important that it is desirable to use every bit of information about it that can be obtained. These 33 additional runs have therefore been discussed at some length in the appendix of this paper, and, suitable corrections for the high side temperatures having been applied, the more favorable of them have been used to get the 77 values of the Joule-Thomson coefficient which are presented in Table IV. These values are plotted in Figure 6 as small black dots. They are more self-consistent than the values in Table IV above, but their trustworthiness is more uncertain as each involves two uncertain corrections of the original data instead of one. They are nevertheless valuable corroborative evidence.

Figure 6 is now complete. The 82 values of the coefficient which are summarized in Tables I., II., and III., lie in the range between 0.6 and 0.7 units of reduced temperature, and form a broad but reasonably well defined band, within which there is no evident tendency for either of the three sets of points to separate themselves from the others. The 118 values of the coefficient which were computed from Dodge's data, and which are presented in Tables IV. and V., lie between 0.7 and 0.9 and form a satisfactory continuation of the band. Above 0.9 are five large circles with diagonal crossbars representing on the same scale the original observations of Joule and Thomson on carbon dioxide, six large circles without crossbars representing Kester's[7] experiments, and one large circle with a horizontal crossbar representing Natanson's[8] result. These circles form a surprisingly good continuation of the curve suggested by the band of steam points. The law of corresponding states is therefore verified for carbon dioxide and water within the limits of error of the observations on the two substances.

The various values in Tables I to V have been grouped according to temperature and averaged. For this purpose a number was assigned

[7] Phys. Zeitsch., 1905, **6**, 44; repeated and revised in Phys. Rev., 1905, **21**, 260.

[8] Wied. Ann., 1887, **31**, 502.

TABLE V.

Summary of Dodge's Main Series of Tests (Corrected as Described).

Test.	Average Pressure		Average Temperature		Reduced Joule-Thomson Coefficient.
	lbs. per sq. in.	Reduced.	Fahr.	Reduced.	
28	328	0.112	558	0.886	0.48
	"	"	534	0.865	0.50
	"	"	503	0.839	0.52
	"	"	430	0.775	0.55
	"	"	463	0.804	0.56
	"	"	574	0.901	0.49
29	380	0.129	568	0.895	0.42
	"	"	544	0.875	0.42
	"	"	520	0.853	0.45
	"	"	483	0.821	0.49
	"	"	460	0.803	0.54
	"	"	504	0.839	0.51
	"	"	538	0.869	0.45
31	330	0.112	511	0.846	0.41
	"	"	474	0.813	0.48
	"	"	441	0.785	0.47
32	379	0.129	558	0.886	0.38
	"	"	540	0.871	0.40
	"	"	524	0.857	0.42
	"	"	507	0.842	0.45
	"	"	493	0.830	0.48
	"	"	469	0.809	0.54
	"	"	444	0.787	0.58
36	385	0.131	563	0.891	0.39
	"	"	539	0.870	0.41
	"	"	516	0.850	0.44
	"	"	491	0.829	0.48
	"	"	460	0.801	0.54
37	338	0.115	571	0.898	0.39
	"	"	545	0.875	0.40
	"	"	516	0.850	0.43
	"	"	480	0.819	0.50
	"	"	456	0.798	0.54
41	205	0.070	562	0.890	0.36
	"	"	527	0.860	0.40
	"	"	462	0.803	0.50
	"	"	432	0.777	0.59
42	255	0.087	565	0.893	0.37
	"	"	540	0.871	0.40
	"	"	515	0.850	0.43
	"	"	492	0.829	0.46
	"	"	459	0.800	0.53
	"	"	437	0.781	0.55

TABLE V — (*continued*).

Test.	Average Pressure		Average Temperature		Reduced Joule-Thomson Coefficient.
	lbs. per sq. in.	Reduced.	Fahr.	Reduced.	
43	302	0.103	550	0.880	0.41
	"	"	533	0.865	0.43
	"	"	514	0.847	0.46
	"	"	495	0.832	0.47
	"	"	468	0.808	0.54
	"	"	444	0.786	0.56
56	256	0.087	513	0.848	0.38
	"	"	475	0.815	0.46
	"	"	435	0.780	0.55
59	252	0.086	560	0.888	0.38
	"	"	531	0.863	0.41
	"	"	488	0.826	0.48
	"	"	441	0.785	0.59
	"	"	463	0.804	0.53
60	204	0.069	500	0.837	0.46
	"	"	470	0.810	0.52
	"	"	431	0.776	0.62
61	168	0.057	493	0.830	0.43
	"	"	464	0.805	0.48
	"	"	432	0.777	0.58
	"	"	400	0.749	0.69
62	200	0.068	569	0.896	0.36
	"	"	513	0.848	0.42
64	302	0.103	550	0.880	0.41
	"	"	526	0.859	0.44
	"	"	493	0.830	0.49
	"	"	467	0.807	0.54
	"	"	436	0.780	0.54
68	166	0.056	485	0.823	0.46
	"	"	449	0.791	0.53
	"	"	409	0.756	0.66
69	162	0.055	483	0.821	0.47
	"	"	446	0.790	0.56
	"	"	406	0.754	0.67

to each of the values in Tables I, II, and III equal to the product of the total number of observations involved at both ends of the determination of the coefficient and the corresponding temperature drop meas-

ured in Centigrade degrees; proportional integral weights from 1 to 6 were then used in forming the weighted means in Table VI. The relative weights of the means themselves which are given in the last column of Table VI are proportional to the square roots of the sums of the above products which entered into each mean; they are given

TABLE VI.

SUMMARY OF WEIGHTED MEANS FROM TABLES I TO V.

Observer.	Temperature Cent.	Temperature Reduced.	Reduced μ'.	Weight.
Grindley	109.4	0.600	1.719	4
	122.3	0.620	1.475	4
	131.0	0.633	1.399	3
	138.6	0.645	1.290	3
	158.4	0.676	1.121	4
	176.2	0.705	0.850	2
Griessmann	128.3	0.628	1.454	2
	134.7	0.646	1.377	5
	152.7	0.667	1.140	5
	167.0	0.690	0.923	4
Peake	120.6	0.616	1.641	1
	137.9	0.644	1.400	2
	160.1	0.679	1.075	4
	179.0	0.708	0.927	6
Dodge				
Table IV.	. . . .	0.770	0.549	(16) [1]
	. . . .	0.870	0.389	(25) [1]
Table V.	. . . .	0.794	0.543	(34) [1]
	. . . .	0.861	0.432	(43) [1]

[1] These are not weights comparable with those above. They give simply the number of observations involved in the corresponding means.

merely as a rough guide for anyone who may wish to use these means for other purposes. If weights had been assigned to Dodge's means on the same basis, they would have been misleadingly large because all the temperature differences retained were large (see the Appendix). The numbers in parentheses in the last column of Table VI are the number of separate coefficients involved in each of the means.

The small figure in the upper corner of Figure 6 is Buckingham's figure (Figure 1 of this paper) replotted on a different scale with the

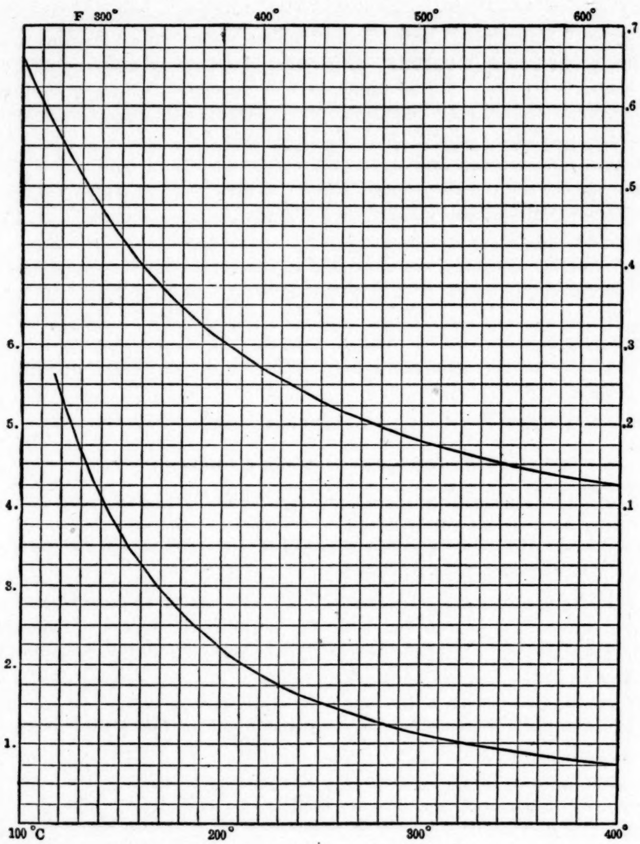

FIGURE 7. Joule-Thomson coefficient in ordinary units. In the lower part of the figure these are Centigrade degrees for a pressure drop of 1 kg. per sq. cm. (scale at left). In the upper part they are Fahrenheit degrees for a pressure drop of 1 lb. per sq. in. (scale at right).

18 means of Table VI added as large circles. The six small circles near t=1 are Kester's carbon dioxide points, the other carbon dioxide points being omitted for clearness. The other points in the figure are easily recognizable on comparison with Figure 1.

Figure 7 shows the smooth curve that best represents the band of Figure 6, translated back from "reduced" to ordinary units, both Centigrade and Fahrenheit. This curve has proved useful in several unexpected ways. For example, it will be made the basis of a discussion of the specific heat of very highly superheated steam in a later paper (see page 292 of these proceedings). It has also made certain cumbersome and uncertain computations in continuous flow calorimetry unnecessary (see "Power," June 2, 1908, page 871). It is hoped that the various scales of Figure 7 are open enough to make the curve useful to others.

All of the observations discussed in this paper have been examined with considerable care, both arithmetically and graphically, for traces of a systematic variation of the Joule-Thomson coefficient with pressure at constant temperature, without success. If such a variation exists even close to the saturation line, it is within the limit of error of the data.

Appendices.

Discussion of Dodge's Data.

In Dodge's apparatus the low side chamber was protected against loss of heat to its surroundings chiefly (although not wholly) by an independently heated steam jacket made in one piece with the wall of the chamber, and kept as nearly as possible at the same temperature as the low side steam. Thermometers were placed in this jacket and their temperatures recorded with the other routine data of each run. As a matter of fact, the jacket temperatures usually ran somewhat lower than the low side steam temperatures, so that some loss of heat by conduction through the chamber wall was to be expected. The high temperatures employed would also tend to make probable some loss of heat by radiation. The possibilities were tested in six special runs numbered 83 to 88, in which the partition between the high and the low side chambers, with its orifice, was completely removed. It was found that the low side thermometers in these tests did read somewhat lower than the high side thermometers although there was no throttling. The 27 observed differences can be fairly well represented by the empirical equation

$$\Delta t = \frac{12\,(\text{low side temp.} - \text{jacket temp.}) + \frac{1}{3}\,(\text{high side temp.})}{\text{flow in lbs. per hour}}.$$

The forms of the two terms in the numerator were intended to correspond to the two sorts of heat loss mentioned above. Corrections corresponding to this formula were accordingly applied to the main

tests. The corrections in the tests summarized in Table IV averaged 2.4° F., and only occasionally amounted to 4°. Those in the tests summarized in Table V averaged 2.9° F. and only occasionally amounted to 5°.

The second set of corrections which are involved in Table V but not in Table IV are much more uncertain. As has been stated, the experiments of the runs of Table V could not be grouped into throttling curves whose various low side points could be combined with each other, all the high side observations being ignored except as indicating constancy of initial conditions, as was done in preparing Table IV. If the data were to be used at all, each low side point had to be taken with its own high side point. When this was done with only the radiation and conduction corrections made, the resulting values of the Joule-Thomson coefficient were not at all self-consistent, the values in each run which corresponded to small temperature drops and therefore to high mean temperatures being abnormally high. This tendency of the points near 0.9 in Figure 6 to swoop upward was unmistakable, and indicated clearly the presence in the tests of Table V of the same "wet steam" error shown in Figure 5 for the tests of Table IV.

The necessary corrections were obtained from the tests of Table IV. It seemed that they alone gave enough of a verification of the law of corresponding states to justify the drawing of a tentative curve like those of Figure 7, and this curve was then used to compute what correction would have to be applied to each of the high side temperatures of the tests of Table IV to make them self-consistent. These corrections were surprisingly constant. They were examined for systematic variations with mean pressure, with pressure drop and with quantity of steam discharged, without success. There seemed, however, to be a slight variation with the mean temperature and the following scheme was adopted:

If the mean reduced temperature is	decrease the high side temperature by
0.9	14°
0.85	13°
0.8	12°
0.75	11°

It should be noticed that these corrections were deduced wholly from the 14 throttling curve tests of Table IV. When they were applied to the tests of Table V, the resulting values of the coefficient showed none of their previous tendency to run high near 0.9, and were

in general much more self-consistent. Further, they now agreed very definitely with the tests of Table IV in verifying the law of corresponding states and lay close along the tentative curve previously drawn. These facts, particularly the disappearance of the tendency to swoop near 0.9, seem to show that this reasoning is not a "circular fallacy," and that the values in Table V are a real corroboration of those in Table IV.

As a precaution against using these corrections too freely in cases where they might, perhaps, not apply, it seemed best to include in Table V only such of the 33 selected tests of the type in question as resembled the tests from which the corrections were determined in having comparatively large steam flow (more than 80 lbs. per hour). Furthermore, all tests or parts of tests were rejected for which the observed temperature drop was not as great as five times the correction, as the application of any correction amounting to more than 20 per cent of the quantity involved seemed unsafe. The 33 tests were thus reduced to 19, and these, corrected as above, gave the 77 values of the coefficient in Table V.

Note on the Vertical Scale of Figure 1.

The numerical values of the ordinates in Figure 1 are not the "reduced" Joule-Thomson effect in the ordinary sense, because Buckingham, in computing them, used 100 in. of mercury as his unit of pressure, but nevertheless expressed his critical pressures in atmospheres. The true reduced values of μ' are those indicated in the upper corner of Figure 6.

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